



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 2702

Inorganics in Marine Sediment

This Standard Reference Material (SRM) is marine sediment collected at the mouth of the Baltimore Harbor, Baltimore, MD. SRM 2702 is intended for use in evaluating analytical methods for the determination of selected elements in marine or fresh water sediment and similar matrices. All of the constituents in SRM 2702, for which certified, reference, and information values are provided, were naturally present in the sediment material before processing. A unit of SRM 2702 consists of a bottle containing 50 g of radiation-sterilized, freeze-dried sediment material.

Certified Concentration Values: Certified values for concentrations, expressed as mass fractions, for 25 elements are provided in Table 1. The certified values are based on the agreement of results from two or more chemically independent analytical techniques obtained at NIST and collaborating expert laboratories [1]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

Reference Concentration Values: Reference values for concentrations, expressed as mass fractions, are provided for eight additional elements in Table 2. Reference values are non-certified values that are the best estimate of the true value. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

Information Concentration Values: Information values for concentrations, expressed as mass fractions, are provided in Table 3 for 11 elements. An information value is considered to be a value that will be of interest and use to the SRM user, but for which insufficient information is available to assess adequately the uncertainty associated with the value, or only a limited number of analyses were performed [1].

Expiration of Certification: The certification of this SRM lot is valid until **01 October 2012**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate. However, the certification is invalid if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The coordination of the technical measurements leading to the certification of this material was under the leadership of R.L. Zeisler of the NIST Analytical Chemistry Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

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See Certificate Revision History on Last Page

Collection and preparation of SRM 2702 were performed by M.P. Cronise and C.N. Fales of the NIST Standard Reference Materials Program and B.J. Porter and M.M. Schantz of the NIST Analytical Chemistry Division.

The sediment material was collected with the assistance of G.G. Lauenstein, J. Collier, and J. Lewis (National Oceanic and Atmospheric Administration).

Consultation on the statistical design of the experimental work and evaluation of the data were provided by M. Vangel and W.S. Liggett, Jr. of the NIST Statistical Engineering Division.

NOTICE AND WARNING TO USERS

Storage: SRM 2702 must be stored in its original bottle at temperatures less than 30 °C away from direct sunlight.

Handling: This material is a naturally occurring marine sediment from an urban area and may contain constituents of unknown toxicity; therefore, caution and care should be exercised during its handling and use.

INSTRUCTIONS FOR USE

Prior to removal of subsamples for analysis, the contents of the bottle should be mixed. The concentrations of constituents in SRM 2702 are reported on a dry-mass basis. The SRM, as received, contains approximately 2.3 % moisture. The sediment sample should be dried to a constant mass before weighing for analysis or a separate subsample of the sediment should be removed from the bottle at the time of analysis and dried to determine the concentration on a dry-mass basis. If the constituents of interest are volatile, then the moisture must be determined with a separate subsample. The drying procedures described below, or equivalent, are recommended; the temperature of 90 °C shall **NOT** be exceeded.

PREPARATION AND ANALYSIS¹

Sample Collection and Preparation: The sediment used to prepare this SRM was collected from the Chesapeake Bay at the mouth of the Baltimore (MD) Harbor near the Francis Scott Key Bridge (39°12.3'N and 76°31.4'W). This location is very near the site where SRM 1941 and SRM 1941a were collected. The sediment was collected using a Kynar-coated modified Van Veen-type grab sampler. A total of approximately 3300 kg of wet sediment was collected from the site. The sediment was freeze-dried, sieved at 70 µm (100 % passing), homogenized in a cone blender, radiation sterilized at 33 kGy to 45 kGy (⁶⁰Co) dose, and then packaged in screw-capped amber glass bottles each containing approximately 50 g.

Conversion to Dry-Mass Basis: The results for the constituents in SRM 2702 are reported on a dry-mass basis; however, the material “as received” contains residual moisture. The amount of moisture in SRM 2702 was determined by measuring the mass loss after freeze drying subsamples of 1.1 g to 1.3 g for four days at 1 Pa with a -10 °C shelf temperature and a -50 °C condenser temperature. The moisture content in SRM 2702 was 2.39 % ± 0.08 % (95 % confidence level). Alternately, drying in a conventional oven was studied. One gram portions were dried at 90 °C for 12 hours and 18 hours; a stable weight was achieved after 18 hours. The measured moisture content was 2.27 % ± 0.09 % (95 % confidence level).

Homogeneity Assessment: The homogeneity of SRM 2702 was assessed by analyzing duplicate samples of approximately 0.1 g from fifteen bottles selected by stratified random sampling. Results from direct determinations by instrumental neutron activation analysis (INAA) and energy-dispersive X-ray fluorescence analysis (ED-XRF) showed observed standard deviations for all reported elements within the precision of the analytical techniques. No statistically significant differences among bottles were observed for the elements at this sample size.

¹Certain commercial equipment, instruments, or materials are identified in this certificate in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Analytical Approach: NIST has a number of analytical techniques available for value assignment. The ones applied to this SRM include dissolution based techniques such as thermal or inductively coupled plasma isotope dilution mass spectrometry (TID-MS or ICP-IDMS) and direct analysis techniques such as INAA, neutron capture prompt gamma activation analysis (PGAA), and radiochemical neutron activation analysis (RNAA). Several of these techniques were also used by collaborating laboratories and complemented by additional dissolution techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) and direct analysis techniques such as wave-length dispersive X-ray fluorescence (WD-XRF) and ED-XRF. Care has been taken to obtain results from both chemically destructive techniques and non-destructive or direct analysis techniques.

Certified Values and Uncertainties: Certified values, derived from the results of several analytical methods performed by NIST and collaborating laboratories (see “Supplemental Information”) and whose combinations differ from element to element, are provided in Table 1. A complete description of the modes of value assignment is given in reference 1. For consistency across elements, a Bayesian statistical model was chosen for computation of certified values and uncertainties [2]. The uncertainty listed with each value is an expanded uncertainty, with coverage factor 2 (approximately 95 % confidence). The reporting follows the ISO/NIST Guides [3].

For each element, there is a NIST result with an uncertainty that is complete in coverage of recognized sources of uncertainties, complemented by results from collaborating laboratories with similarly complete uncertainties, and usually several results without complete uncertainties. The uncertainties of the latter results were augmented on the basis of the differences among the results obtained by different methods [4]. The Bayesian methods combine results by different methods from different laboratories according to the results provided and the uncertainties provided with them. Thus, a consistent methodology was used for all elements.

Table 1. Certified Concentrations for Selected Elements

Elements	Mass Fraction mg/kg (unless noted as %)			Elements	Mass Fraction mg/kg (unless noted as %)		
Al ^{b,c,f,G}	8.41 %	±	0.22 %	Ni ^{A,a,b,c,d,e}	75.4	±	1.5
As ^{b,c,d,G}	45.3	±	1.8	P ^{b,c,f,H}	0.1552 %	±	0.0066 %
Ba ^{A,b,e}	397.4	±	3.2	Pb ^{A,a,b,c,e}	132.8	±	1.1
Ce ^{b,c,e,G}	123.4	±	5.8	Rb ^{b,e,G}	127.7	±	8.8
Cd ^{A,a,b,d,I}	0.817	±	0.011	Sb ^{a,b,e,G}	5.60	±	0.24
Co ^{b,c,G}	27.76	±	0.58	Sc ^{b,c,G}	25.9	±	1.1
Cr ^{a,b,c,e,G}	352	±	22	Sr ^{A,b,c,e}	119.7	±	3.0
Fe ^{b,c,f,G}	7.91 %	±	0.24 %	Th ^{b,c,e,G}	20.51	±	0.96
Hg ^{A-1,d,H}	0.4474	±	0.0069	Ti ^{b,c,f,G}	0.884 %	±	0.082 %
K ^{b,c,f,G}	2.054 %	±	0.072 %	Tl ^{A,a}	0.8267	±	0.0060
La ^{b,c,e,G}	73.5	±	4.2	V ^{b,c,G}	357.6	±	9.2
Mn ^{b,c,G}	1757	±	58	Zn ^{a,b,c,e,G}	485.3	±	4.2
Na ^{b,c,f,G}	0.681 %	±	0.020 %				

Supplemental Information: Analytical Techniques Used for Certified Values in Table 1 (Superscript uppercase letters indicate methods used by NIST)

- A, a Inductively coupled plasma isotope dilution mass spectrometry (ICP-IDMS)
- A-1 Cold vapor ICP-IDMS
- b Inductively coupled plasma mass spectrometry (ICP-MS)
- c Inductively coupled plasma atomic emission spectrometry (ICP-AES)
- d Atomic absorption spectrometry including hydride generation and cold vapor techniques (AAS)
- e Energy dispersive X-ray fluorescence (ED-XRF)
- f Wave-length dispersive X-ray fluorescence (WD-XRF)
- G Instrumental neutron activation analysis (INAA)
- H Radiochemical neutron activation analysis (RNAA)
- I Prompt gamma activation analysis (PGAA)

Reference Values and Uncertainties: Reference values are based on results from one method carried out in several laboratories or from two or more analytical methods without NIST results. The Bayesian methods of combining the results by different methods from different laboratories were applied as above. These results do not fulfill the criteria for certification since a full estimate of method bias or results from NIST methods have not been available. The reporting follows the ISO/NIST Guides [3].

Table 2. Reference Values for Concentrations of Selected Elements

Elements	Mass Fraction mg/kg (unless noted as %)	Elements	Mass Fraction mg/kg (unless noted as %)
Ag ^{a,d}	0.622 ± 0.078	Mg ^{b,c,f}	0.990 % ± 0.074 %
Ca ^{b,c,f}	0.343 % ± 0.024 %	Mo ^{b,c,e}	10.8 ± 1.6
Cu ^{a,b,c,d,e}	117.7 ± 5.6	Se ^{b,c,e}	4.95 ± 0.46
Ga ^{b,c,e}	24.3 ± 1.9	Sn ^{a,c,e}	31.6 ± 2.4

Supplemental Information: Analytical Techniques Used for Reference Values in Table 2

- ^a Inductively coupled plasma isotope dilution mass spectrometry (ICP-IDMS)
- ^b Inductively coupled plasma mass spectrometry (ICP-MS)
- ^c Inductively coupled plasma atomic emission spectrometry (ICP-AES)
- ^d Atomic absorption spectrometry including hydride generation and cold vapor techniques (AAS)
- ^e Energy dispersive X-ray fluorescence (ED-XRF)
- ^f Wave-length dispersive X-ray fluorescence (WD-XRF)

Information Values: Information values are given in SRM 2702 to assist users in the assays of non-certified elements. Information values are based on results that did not allow complete assessment of all sources of uncertainty, hence, only estimated means without uncertainties are given.

Table 3. Information Values for Selected Elements

Elements	Mass Fraction mg/kg (unless noted as %)	Elements	Mass Fraction mg/kg (unless noted as %)
Be ^{b,c}	3.0	Nb ^{c,e}	63
C (total) ^j	3.36 %	Nd ^G	56
C (organic) ^j	3.27 %	S ^j	1.5 %
Cs ^{b,G}	7.1	Sm ^G	10.8
Hf ^G	12.6	U ^{b,e}	10.4
Li ^{b,c}	78.2	W ^G	6.2

Supplemental Information: Analytical Techniques Used for Information Values in Table 3 (Superscript uppercase letter G indicates method used by NIST)

- ^b Inductively coupled plasma mass spectrometry (ICP-MS)
- ^c Inductively coupled plasma atomic emission spectrometry (ICP-AES)
- ^e Energy dispersive X-ray fluorescence (ED-XRF)
- ^G Instrumental neutron activation analysis (INAA)
- ^j Combustion techniques

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REFERENCES

- [1] May, W.E.; Gills, T.E.; Parris, R.; Beck, II, C.M.; Fassett, J.D.; Gettings, R.J.; Greenberg, R.R.; Guenther, F.R.; Kramer, G.; MacDonald, B.S.; Wise, S.A.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 (1999); available at <http://www.cstl.nist.gov/nist839/srminfo.html>.
- [2] Gelman, A.; Carlin, J.B.; Stern, H.S.; Rubin, D.R.; *Bayesian Data Analysis*; Chapman & Hall: London (1995).
- [3] *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st Ed.; ISO, Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <http://physics.nist.gov/Pubs/>.
- [4] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.K.; Vangel, M.G.; Yen, J.H.; Zhang N.F.; *An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM*; J.Res. National Institute of Standards and Technology 105, pp. 571-579 (2000).

Certificate Revision History: 07 January 2004 (This revision reflects a corrected Cu reference value in Table 2, an updated Hg certified value and uncertainty in Table I, and editorial revisions.); 03 December 2002 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet <http://www.nist.gov/srm>.